



TITLE OF THE INVENTION

SEMICONDUCTOR DEVICE AND METHOD OF MANUFACTURING THE  
SAME

5 BACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention relates to a semiconductor  
device and a method of manufacturing the same and, more  
particularly, to the technology that is suitable for  
10 preventing the diffusion of the copper of the copper  
wiring layer.

2. Description of the Related Art

In recent years, in order to increase the operations<sup>2</sup>  
speed of the semiconductor element such as <sup>2</sup>LSI, etc.,  
15 ~~such a structure is gradually employed that the~~  
<sup>2</sup>  
20 insulating film having the low dielectric constant  
(referred to as <sup>2</sup>the "low dielectric constant film"  
hereinafter) is formed on the copper wiring layer as the  
interlayer insulating film. In this structure, the low  
dielectric constant film is formed on the copper wiring  
20 layer as an interlayer insulating film, and then <sup>a</sup>the via  
hole is formed in this low dielectric constant film to  
expose the copper wiring layer. In forming this via hole,  
<sup>a</sup>  
25 the block insulating film is formed on the copper wiring  
layer in advance, and then the interlayer insulating film  
is formed on this block insulating film. The block  
insulating film serves as an etching stopper film when

etching the interlayer insulating film. The block insulating serves also as a copper diffusion preventing film, which prevents copper contained in the copper wiring layer from diffusing into the interlayer insulating film.

In the prior art, <sup>2</sup>the silicon nitride film (referred to as the "SiN film" hereinafter), which is superior in preventing the copper diffusion, is used for the block insulating film.

SiN film, however, has a problem <sup>in</sup> that it lowers the operation <sup>2</sup>speed of the semiconductor device due to its high dielectric constant (about 7).

<sup>as a substitute for</sup>  
~~other than~~ the SiN film, <sup>2/30</sup>[some] low dielectric constant films <sup>2</sup>are known to be used for the block

insulating film. These low dielectric constant films are formed using <sup>2</sup>CVD method (Chemical Vapor Deposition

method), and the reaction gases for this method is that consists of methylsilane ( $\text{Si}(\text{CH}_3)_4$ ) and  $\text{CH}_4$  or that

consists of organic silane and  $\text{CH}_4$ . These methods; however, are problematic because a large number of Si-C bonds are formed in the low dielectric constant film. Since the Si-C bonds increases the leakage current in the film, the block film formed as above has the problem that the leakage current is large.

#### SUMMARY OF THE INVENTION

It is an object of the present invention to provide

a novel semiconductor device capable of preventing the diffusion of the copper <sup>from</sup> in the copper wiring layer and a method of manufacturing the same. ✓

5 According to the semiconductor device manufacturing method of the present invention, <sup>a</sup> the process gas containing any one of  $N_2$  and  $N_2O$  is <sup>converted to a plasma</sup> plasmanized and then the surface of the copper wiring layer is exposed to the <sup>plasma</sup> plasmanized process gas. <sup>a</sup> Alternatively, the process gas containing  $N_2$  and  $NH_3$  may be <sup>used to form the plasma</sup> plasmanized in place of above gas and then the surface of the copper wiring layer may be exposed to this plasmanized process gas. ✓

10 According to the examination result, <sup>has been</sup> It <sup>was</sup> discovered that <sup>2</sup> the surface layer portion of the copper wiring layer <sup>is</sup> was reformed by these plasma processes and such surface layer portion could function <sup>2</sup> as the copper diffusion preventing layer. This means that the copper wiring layer itself has the function of preventing the diffusion of copper. Therefore, <sup>2</sup> the high <sup>cap</sup> ability of <sup>for</sup> preventing copper diffusion is not required for the copper diffusion preventing film (the block insulating film, etc.) formed on the copper wiring layer. etc. ✓

20 Therefore, there is no need to use the high dielectric films (SiN film <sup>or</sup> and like) of the prior art, which are considered to have a superior ability <sup>to</sup> of preventing the copper diffusion.

25

Accordingly, in the present invention, films having <sup>2</sup> relatively low dielectric constant can be formed on the

copper wiring layer, in place of the high dielectric constant film in the prior art. Example<sup>s</sup> of the films having <sup>such a</sup> ~~the~~ relatively low dielectric constant <sup>are</sup> ~~is~~ the silicon-containing insulating film<sup>s</sup> such as a SiOCH film, a SiO film, a SiONCH film, a SiCH film, a SiCNH film, and the like. If the high dielectric constant is not problematic, however, <sup>a</sup> ~~the~~ SiN film may be employed. ✓

The so-called damascene structure may be formed on this silicon-containing insulating film. In order to obtain the damascene structure, the interlayer insulating film is <sup>a</sup> formed on the silicon-containing insulating film, then ~~the~~ via hole is formed in the silicon-containing insulating film and the interlayer insulating film, then <sup>a</sup> ~~the~~ plug connected electrically to the copper wiring layer is buried in the via hole, and ~~the~~ upper wiring connected electrically to the plug is formed on the interlayer insulating film. As described above, since the surface layer portion of the copper wiring layer is reformed to function as the copper diffusion preventing layer, the diffusion of the copper into the silicon-containing insulating film and the interlayer insulating film <sup>is</sup> ~~can be~~ prevented. ✓ ✓ ✓

Moreover, if the surface of this copper wiring layer is exposed to the NH<sub>3</sub> plasma before the surface layer portion of the copper wiring layer is reformed, the natural oxide film formed on the surface of the copper wiring can be removed. If the natural oxide film is

removed in this manner, the film formed on the copper wiring layer becomes difficult to peel off from the copper wiring layer.

Furthermore, instead of reforming the surface portion of the copper wiring in the above manner, a silicon-containing insulating film may be formed on the copper wiring layer which <sup>has</sup> ~~is~~ <sup>been</sup> ~~not~~ subjected to the above-described reforming process. In this case, after forming the silicon-containing insulating film, process gas containing at least one of  $\text{NH}_3$ ,  $\text{N}_2$ , and  $\text{N}_2\text{O}$  is <sup>converted to a plasma</sup> ~~plasmanized~~ and then the surface of the silicon-containing insulating film is exposed to the <sup>plasma</sup> ~~above plasmanized~~ process gas. <sup>It has been</sup> ~~According to the examination result, it was~~ discovered that the silicon-containing insulating film <sup>is</sup> ~~was~~ reformed by this plasma process and <sup>that reformed</sup> ~~the~~ silicon-containing insulating film <sup>is</sup> ~~had the~~ function <sup>as</sup> ~~the~~ copper diffusion preventing film.

<sup>may be</sup> ~~As~~ the silicon-containing insulating film to be reformed, there are a  $\text{SiOCH}$  film, a  $\text{SiO}$  film, a  $\text{SiN}$  film; a  $\text{SiONCH}$  film, a  $\text{SiCH}$  film, a  $\text{SiCNH}$  film, <sup>or</sup> ~~and~~ the like. <sup>For example.</sup> Among these films, the  $\text{SiOCH}$  film and the  $\text{SiONCH}$  film can be formed by ~~the~~ chemical vapor deposition <sup>method</sup> using <sup>the</sup> reaction gas that contains a compound having <sup>a</sup> ~~a~~ siloxane bonds. If <sup>the</sup> ~~the~~ compound having <sup>the</sup> ~~the~~ siloxane bonds is employed, <sup>a</sup> ~~the~~  $\text{SiOCH}$  film <sup>or a</sup> ~~and the~~  $\text{SiONCH}$  film <sup>which has a</sup> ~~that have the~~ low dielectric constant and <sup>which</sup> ~~suppress~~ the leakage current can be formed. As a result,

with  
 [in] the SiOCH film and [in] the SiONCH film, there <sup>is</sup> [exists] no  
 problem that the leakage current <sup>will be</sup> increased <sup>as</sup> like in the  
 prior art <sup>or</sup> [and] that the operation <sup>will be</sup> speed of the  
 semiconductor device <sup>of</sup> slows due to the high dielectric  
 constant [like in] the SiN film.

The so-called damascene structure may also be  
 formed on the silicon-containing insulating film that is  
 reformed in this manner. In order to obtain [the] <sup>a</sup>  
 damascene structure, [the] <sup>an</sup> interlayer insulating film is  
 10 formed on the reformed silicon-containing insulating film,  
 then [the] <sup>a</sup> via hole is formed in the silicon-containing  
 insulating film and the interlayer insulating film, then  
 [the] <sup>a</sup> plug connected electrically to the copper wiring  
 layer is buried in the via hole, and then [the] upper  
 15 wiring connected electrically to the plug is formed on  
 the interlayer insulating film. As described above,  
 since the reformed silicon-containing insulating film can  
 function as the copper diffusion preventing film, the  
 copper can be prevented from diffusing into the silicon-  
 20 containing insulating film and into the interlayer  
 insulating film.

#### BRIEF DESCRIPTION OF THE DRAWINGS

FIG.1 is a sectional view showing the semiconductor  
 25 manufacturing <sup>apparatus</sup> [equipment] employed in an embodiment of the  
 present invention;

FIGS.2A to 2C are sectional views showing steps of

manufacturing a semiconductor device according to a first

[method of the] embodiment of the present invention;

FIG.3 is a graph <sup>of content</sup> [showing SIMS examination results] <sup>of</sup> [about] the elements [that are] contained in the silicon-  
 5 containing insulating film <sup>as determined by SIMS examination,</sup> immediately after the film  
 formation, <sup>versus depth</sup> in the first [method of the] embodiment of the  
<sup>method of the</sup> present invention;

FIG.4 is a graph <sup>of content</sup> [showing SIMS examination results] <sup>of</sup> [about] the elements [that are] contained in the silicon-  
 10 containing insulating film <sup>as determined by SIMS,</sup> after the  
 [when such] silicon-containing  
 insulating film is annealed in vacuum at 500 °C for 4  
 hours, <sup>versus depth</sup> in the first [method of the] embodiment of the  
<sup>method of the</sup> present invention;

FIG.5 is a graph <sup>of content</sup> [showing SIMS examination results] <sup>of</sup> [about] the elements [that are] contained in the silicon-  
 15 containing insulating film immediately after the film  
 formation, <sup>versus depth</sup> when the N<sub>2</sub> plasma <sup>treatment</sup> [process] is <sup>omitted</sup> [not executed];

FIG.6 is a graph <sup>of content</sup> [showing SIMS examination results] <sup>of</sup> [about] the elements [that are] contained in the silicon-  
 20 containing insulating film which is not subjected to the  
 N<sub>2</sub> plasma <sup>treatment, but which</sup> [process] when such silicon-containing insulating  
 [film] is annealed in vacuum at 500 °C for 4 hours after the  
 film formation;

FIGS.7A to 7C are sectional views showing steps of  
 25 manufacturing a semiconductor device according to a  
 second [method of the] embodiment of the <sup>method of the</sup> present invention;

FIG.8 is a graph <sup>of content</sup> [showing SIMS examination results]

<sup>of</sup>  
 [about] the elements [that are] contained in the silicon-  
 containing insulating film when such silicon-containing  
 insulating film is annealed in vacuum at 450 °C for 4  
 hours after the film formation, in the second [method of]  
 5 [the] embodiment of the <sup>method of the</sup> present invention;

FIG.9 is a sectional view <sup>illustrating</sup> [showing] a sectional  
 [structure used to] measure <sup>ment of</sup> the leakage current of the  
 [silicon- containing] insulating film, in the second [method]  
 [of the] <sup>method of the</sup> embodiment of the present invention;

10 FIG.10 is a graph showing the leakage current of the  
 silicon-containing insulating film when the NH<sub>3</sub> plasma  
 process is performed for the silicon-containing  
 insulating film immediately after the film formation, in  
 the second [method of the] <sup>method of the</sup> embodiment of the present  
 15 invention;

FIG.11 is a graph showing the leakage current of the  
 silicon-containing insulating film after such silicon-  
 containing insulating film is subjected to the NH<sub>3</sub> plasma  
 process and is then annealed, in the second [method of the]  
 20 embodiment of the <sup>method of the</sup> present invention; and

FIGS.12A to 12H are sectional views showing <sup>application of</sup> [the case]  
 [where] the present invention [is applied] to the damascene  
 method.

## 25 DESCRIPTION OF THE PREFERRED EMBODIMENTS

Next, <sup>preferred</sup> [an] embodiment of the present invention will be  
 explained with reference to the accompanying drawings



hereinafter.

[(1)] Explanation of the semiconductor manufacturing apparatus equipment employed in the preferred present embodiment

FIG.1 is a sectional view showing the semiconductor manufacturing apparatus equipment employed in the preferred present embodiment.

In FIG.1, 101 denotes a chamber in which the film formation and the plasma process are carried out. Provided in the chamber 101 are two opposing electrodes, i.e., a lower electrode 102 and an upper electrode 104. The lower and upper electrodes 102, 104 both have an almost circular planar shape whose diameter is about 230 mm.

The lower electrode 102 is also used as a loading table on which a substrate 103 is loaded. A heater (not shown) for heating the substrate 103 up to a desired temperature is built in to this lower electrode 102. In FIG.1, 105 denotes a power supplying wiring for supplying a power to the heater.

In addition, the upper electrode 104 is also used as a shower head for supplying a gas into the chamber 101.

A first high frequency power supply 107 and a second high frequency power supply 109 are connected to these two electrodes 104, 102 respectively. The gas in the chamber 101 can be converted to a plasma by applying a high frequency power to the gas from one or both of these high frequency power supplies 107, 109.

A gas introducing port 108 is provided <sup>in</sup> to the upper electrode 104, and the gas is introduced into the chamber 101 through the gas introducing port 108. An exhaust port 106 is provided <sup>for</sup> to the chamber 101, and the gas introduced into the chamber 101 is exhausted via the port 106 to reduce the pressure in the chamber 101.

<sup>Preferred embodiments of</sup>  
 [(2)] Explanation of a semiconductor device manufacturing method according to the embodiment of the present invention

Next, the semiconductor device manufacturing method according to the present embodiment will be explained hereunder. In order to manufacture the semiconductor device by the present embodiment, there are first and second methods described as follows.

[(1)] First method embodiment

Firstly, the first method will be explained with reference to FIGS. 2A to 2C hereunder.

In this <sup>first embodiment</sup> method, as shown in FIG. 2A, substrate 103 is loaded on the lower electrode 102 (see FIG. 1). The substrate 103 <sup>consists of</sup> is constructed by forming a copper wiring layer 110 <sup>formed</sup> on an underlying insulating film 112 such as SiO<sub>2</sub> film, or the like, <sup>which, in turn,</sup> [The underlying insulating film 112] is formed on <sup>2</sup> the silicon substrate (not shown).

Then, as shown in FIG. 2B, <sup>the</sup> a surface of the copper wiring layer 110 is <sup>contacted</sup> processed with <sup>the</sup> plasma and reformed. This process is carried out <sup>under the</sup> in accordance with following conditions A.

(Conditions A)

- temperature of the substrate 103<sup>°</sup> ~~an~~ 375 °C
- pressure in the chamber 101<sup>°</sup> ~~A~~ 0.5 to 1.0 Torr
- frequency of the first high frequency power supply  
107<sup>°</sup> ~~an~~ 13.56 MHz
- power of the first high frequency power supply  
107<sup>°</sup> ~~A~~ 0 W (not applied)
- frequency of the second high frequency power supply  
109<sup>°</sup> ~~an~~ 380 KHz
- power of the second high frequency power supply  
109<sup>°</sup> ~~an~~ 150 W
- process time ~~an~~ 30 sec
- process gas flow rate ~~an~~ see Table 1

Table 1

	Process gas	gas flow rate (sccm)			
		N <sub>2</sub>	N <sub>2</sub> O	NH <sub>3</sub>	C <sub>x</sub> H <sub>y</sub>
15	① N <sub>2</sub>	100	---	---	---
	② N <sub>2</sub> +N <sub>2</sub> O	200	100	---	---
	③ N <sub>2</sub> +NH <sub>3</sub>	200	---	100	---
20	④ N <sub>2</sub> +C <sub>x</sub> H <sub>y</sub>	200	---	---	100
	⑤ N <sub>2</sub> O+C <sub>x</sub> H <sub>y</sub>	---	100	---	200
	⑥ N <sub>2</sub> +N <sub>2</sub> O+C <sub>x</sub> H <sub>y</sub>	100	100	---	100

As shown in Table 1, there are six types ① to ⑥ <sup>of</sup> the process gas. <sup>At least</sup> [Any] one of N<sub>2</sub> and N<sub>2</sub>O is contained in <sup>each of the</sup> [all] process gases. These gases are <sup>converted to plasma</sup> plasmanized in the chamber 101. In this case, NH<sub>3</sub> may be added as in the case of process gas ③, and C<sub>x</sub>H<sub>y</sub> (hydrocarbon) may be added as in the cases

of the process gases ④ to ⑥. Specific examples of the  $C_xH_y$  hydrocarbons are  $CH_4$  and  $C_2H_2$ . It is postulated that if  $C_xH_y$  is added, a thin film made of  $C_xH_y$  is formed on the surface of the copper wiring layer 110. <sup>and</sup> <sup>rendered</sup> it is <sup>believed</sup> expected that the copper wiring layer 110 is <sup>rendered</sup> difficult to be etched ~~in~~ the later steps by this thin film.

Then, as shown in FIG.2C, a silicon-containing insulating film 111 is formed on the copper wiring layer 110. This silicon-containing insulating film 111 is formed by the plasma CVD method (Chemical Vapor Deposition method) in <sup>under</sup> <sup>the</sup> accordance with following conditions B.

(Conditions B)

- temperature of the substrate 103: ~~100~~ 375 °C
- 15 • pressure in the chamber 101: ~~10~~ 1.0 Torr
- frequency of the first high frequency power supply 107: ~~10~~ 13.56 MHz
- power of the first high frequency power supply 107: ~~10~~ 0 W (not applied)
- 20 • frequency of the second high frequency power supply 109: ~~10~~ 380 KHz
- power of the second high frequency power supply 109: ~~10~~ 100 to 150 W
- deposited film thickness ~~10~~ 100 nm
- 25 • gas flow rate ~~10~~ see Table 2

Table 2

Type of silicon- Containing Insulating film 111	gas flow rate (sccm)					
	HMDSO (Si(CH <sub>3</sub> ) <sub>4</sub> )	TMS	SiH <sub>4</sub>	N <sub>2</sub> O	NH <sub>3</sub>	CH <sub>4</sub>
5	① SiOCH	50	---	---	---	100
	② SiO	---	50	---	100	---
	③ SiN	---	---	50	100	---
	④ SiONCH	50	---	---	200	100
10	⑤ SiCH	---	50	---	---	100
	⑥ SiCNH	---	50	---	---	200

As shown in Table 2, there are an SiOCH film, an SiO film, an SiN film, an SiONCH film, an SiCH film, and an SiCNH film <sup>can be formed as</sup> as the type of the silicon-containing insulating film 111 to be formed. These films can be formed by combining together the gases in Table 2. In the present invention, any one of these films may be formed employed. It should be noted that when the type of the film is denoted as "SiXYZ film", this film should be 15 is understood <sup>to</sup> as containing at least an Si element, an X element, a Y element, and a Z element.

In Table 2, HMDSO (hexamethyldisiloxane: (Si(CH<sub>3</sub>)<sub>3</sub>)<sub>2</sub>O) is liquid at the room temperature (20 °C). ~~X~~ The flow rate of the liquid HMDSO is adjusted by the liquid massflow meter (not shown), and then the liquid HMDSO is vaporized by heating and then <sup>the vapor</sup> is introduced into the chamber 101. Alternatively, in place of this process, 25

the liquid HMDSO may be <sup>first</sup> vaporized, then the flow rate of the vaporized HMDSO may be adjusted by the high-temperature mass flow meter (not shown), and then the vaporized HMDSO may be supplied to the chamber 101. The flow rate of the HMDSO <sup>under</sup> in the conditions B is <sup>that</sup> those obtained when the HMDSO is vaporized in the above manner.

In particular, the dielectric constant of the SiOCH film, which was formed by using the HMDSO under the conditions B, was about 4.0. This value is lower than the dielectric constant of the SiN film. Furthermore, if the HMDSO is used, since Si (silicon) in the HMDSO is already bonded to O (oxygen) in the form of siloxane bonds (Si-O-Si), the Si-C bonds are <sup>reduced</sup> not so much contained in the SiOCH film. As a result, the SiOCH film <sup>has a low</sup> dielectric constant thereof is low as explained above, becomes a <sup>and a suppressed</sup> film whose leakage current is suppressed. This is also the case for the SiONCH film that is formed by using the HMDSO. <sup>has been mentioned as a</sup>

The HMDSO is the compound having the siloxane bonds, but the <sup>the</sup> similar advantage to the above can be obtained when any one of <sup>the</sup> following compounds having the siloxane bonds is employed in place of the HMDSO.

OMCTS (octamethylcyclotetrasiloxane :  $(\text{Si}(\text{CH}_3)_2)_4\text{O}_4$ )

HEDS (hexaethyldisiloxane :  $(\text{Si}(\text{C}_2\text{H}_5)_3)_2\text{O}$ )

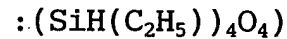
25 TMDS (tetramethyldisiloxane :  $(\text{SiH}(\text{CH}_3)_2)_2\text{O}$ )

TEDS (tetraethyldisiloxane :  $(\text{SiH}(\text{C}_2\text{H}_5)_2)_2\text{O}$ )

TMCTS (tetramethylcyclotetrasiloxane



TECTS (tetraethylcyclotetrasiloxane



5 If any one of these compounds is employed, the silicon- containing insulating film 111 <sup>with a suppressed</sup> [whose] leakage current <sup>and having a</sup> [is] suppressed and which has <sup>the</sup> low dielectric constant can be formed.

Also, as shown in Table 2, the organic silane <sup>1</sup> TMS (tetramethylsilane :  $\text{Si}(\text{CH}_3)_4$ ) <sup>2</sup> is employed to form the SiO film, the SiCH film, and the SiCNH film, but other organic silane may be employed in place of TMS. <sup>3</sup> <sup>4</sup> <sup>5</sup> <sup>6</sup> <sup>7</sup> <sup>8</sup> <sup>9</sup> <sup>10</sup> <sup>11</sup> <sup>12</sup> <sup>13</sup> <sup>14</sup> <sup>15</sup> <sup>16</sup> <sup>17</sup> <sup>18</sup> <sup>19</sup> <sup>20</sup> <sup>21</sup> <sup>22</sup> <sup>23</sup> <sup>24</sup> <sup>25</sup> <sup>26</sup> <sup>27</sup> <sup>28</sup> <sup>29</sup> <sup>30</sup> <sup>31</sup> <sup>32</sup> <sup>33</sup> <sup>34</sup> <sup>35</sup> <sup>36</sup> <sup>37</sup> <sup>38</sup> <sup>39</sup> <sup>40</sup> <sup>41</sup> <sup>42</sup> <sup>43</sup> <sup>44</sup> <sup>45</sup> <sup>46</sup> <sup>47</sup> <sup>48</sup> <sup>49</sup> <sup>50</sup> <sup>51</sup> <sup>52</sup> <sup>53</sup> <sup>54</sup> <sup>55</sup> <sup>56</sup> <sup>57</sup> <sup>58</sup> <sup>59</sup> <sup>60</sup> <sup>61</sup> <sup>62</sup> <sup>63</sup> <sup>64</sup> <sup>65</sup> <sup>66</sup> <sup>67</sup> <sup>68</sup> <sup>69</sup> <sup>70</sup> <sup>71</sup> <sup>72</sup> <sup>73</sup> <sup>74</sup> <sup>75</sup> <sup>76</sup> <sup>77</sup> <sup>78</sup> <sup>79</sup> <sup>80</sup> <sup>81</sup> <sup>82</sup> <sup>83</sup> <sup>84</sup> <sup>85</sup> <sup>86</sup> <sup>87</sup> <sup>88</sup> <sup>89</sup> <sup>90</sup> <sup>91</sup> <sup>92</sup> <sup>93</sup> <sup>94</sup> <sup>95</sup> <sup>96</sup> <sup>97</sup> <sup>98</sup> <sup>99</sup> <sup>100</sup> <sup>101</sup> <sup>102</sup> <sup>103</sup> <sup>104</sup> <sup>105</sup> <sup>106</sup> <sup>107</sup> <sup>108</sup> <sup>109</sup> <sup>110</sup> <sup>111</sup> <sup>112</sup> <sup>113</sup> <sup>114</sup> <sup>115</sup> <sup>116</sup> <sup>117</sup> <sup>118</sup> <sup>119</sup> <sup>120</sup> <sup>121</sup> <sup>122</sup> <sup>123</sup> <sup>124</sup> <sup>125</sup> <sup>126</sup> <sup>127</sup> <sup>128</sup> <sup>129</sup> <sup>130</sup> <sup>131</sup> <sup>132</sup> <sup>133</sup> <sup>134</sup> <sup>135</sup> <sup>136</sup> <sup>137</sup> <sup>138</sup> <sup>139</sup> <sup>140</sup> <sup>141</sup> <sup>142</sup> <sup>143</sup> <sup>144</sup> <sup>145</sup> <sup>146</sup> <sup>147</sup> <sup>148</sup> <sup>149</sup> <sup>150</sup> <sup>151</sup> <sup>152</sup> <sup>153</sup> <sup>154</sup> <sup>155</sup> <sup>156</sup> <sup>157</sup> <sup>158</sup> <sup>159</sup> <sup>160</sup> <sup>161</sup> <sup>162</sup> <sup>163</sup> <sup>164</sup> <sup>165</sup> <sup>166</sup> <sup>167</sup> <sup>168</sup> <sup>169</sup> <sup>170</sup> <sup>171</sup> <sup>172</sup> <sup>173</sup> <sup>174</sup> <sup>175</sup> <sup>176</sup> <sup>177</sup> <sup>178</sup> <sup>179</sup> <sup>180</sup> <sup>181</sup> <sup>182</sup> <sup>183</sup> <sup>184</sup> <sup>185</sup> <sup>186</sup> <sup>187</sup> <sup>188</sup> <sup>189</sup> <sup>190</sup> <sup>191</sup> <sup>192</sup> <sup>193</sup> <sup>194</sup> <sup>195</sup> <sup>196</sup> <sup>197</sup> <sup>198</sup> <sup>199</sup> <sup>200</sup> <sup>201</sup> <sup>202</sup> <sup>203</sup> <sup>204</sup> <sup>205</sup> <sup>206</sup> <sup>207</sup> <sup>208</sup> <sup>209</sup> <sup>210</sup> <sup>211</sup> <sup>212</sup> <sup>213</sup> <sup>214</sup> <sup>215</sup> <sup>216</sup> <sup>217</sup> <sup>218</sup> <sup>219</sup> <sup>220</sup> <sup>221</sup> <sup>222</sup> <sup>223</sup> <sup>224</sup> <sup>225</sup> <sup>226</sup> <sup>227</sup> <sup>228</sup> <sup>229</sup> <sup>230</sup> <sup>231</sup> <sup>232</sup> <sup>233</sup> <sup>234</sup> <sup>235</sup> <sup>236</sup> <sup>237</sup> <sup>238</sup> <sup>239</sup> <sup>240</sup> <sup>241</sup> <sup>242</sup> <sup>243</sup> <sup>244</sup> <sup>245</sup> <sup>246</sup> <sup>247</sup> <sup>248</sup> <sup>249</sup> <sup>250</sup> <sup>251</sup> <sup>252</sup> <sup>253</sup> <sup>254</sup> <sup>255</sup> <sup>256</sup> <sup>257</sup> <sup>258</sup> <sup>259</sup> <sup>260</sup> <sup>261</sup> <sup>262</sup> <sup>263</sup> <sup>264</sup> <sup>265</sup> <sup>266</sup> <sup>267</sup> <sup>268</sup> <sup>269</sup> <sup>270</sup> <sup>271</sup> <sup>272</sup> <sup>273</sup> <sup>274</sup> <sup>275</sup> <sup>276</sup> <sup>277</sup> <sup>278</sup> <sup>279</sup> <sup>280</sup> <sup>281</sup> <sup>282</sup> <sup>283</sup> <sup>284</sup> <sup>285</sup> <sup>286</sup> <sup>287</sup> <sup>288</sup> <sup>289</sup> <sup>290</sup> <sup>291</sup> <sup>292</sup> <sup>293</sup> <sup>294</sup> <sup>295</sup> <sup>296</sup> <sup>297</sup> <sup>298</sup> <sup>299</sup> <sup>300</sup> <sup>301</sup> <sup>302</sup> <sup>303</sup> <sup>304</sup> <sup>305</sup> <sup>306</sup> <sup>307</sup> <sup>308</sup> <sup>309</sup> <sup>310</sup> <sup>311</sup> <sup>312</sup> <sup>313</sup> <sup>314</sup> <sup>315</sup> <sup>316</sup> <sup>317</sup> <sup>318</sup> <sup>319</sup> <sup>320</sup> <sup>321</sup> <sup>322</sup> <sup>323</sup> <sup>324</sup> <sup>325</sup> <sup>326</sup> <sup>327</sup> <sup>328</sup> <sup>329</sup> <sup>330</sup> <sup>331</sup> <sup>332</sup> <sup>333</sup> <sup>334</sup> <sup>335</sup> <sup>336</sup> <sup>337</sup> <sup>338</sup> <sup>339</sup> <sup>340</sup> <sup>341</sup> <sup>342</sup> <sup>343</sup> <sup>344</sup> <sup>345</sup> <sup>346</sup> <sup>347</sup> <sup>348</sup> <sup>349</sup> <sup>350</sup> <sup>351</sup> <sup>352</sup> <sup>353</sup> <sup>354</sup> <sup>355</sup> <sup>356</sup> <sup>357</sup> <sup>358</sup> <sup>359</sup> <sup>360</sup> <sup>361</sup> <sup>362</sup> <sup>363</sup> <sup>364</sup> <sup>365</sup> <sup>366</sup> <sup>367</sup> <sup>368</sup> <sup>369</sup> <sup>370</sup> <sup>371</sup> <sup>372</sup> <sup>373</sup> <sup>374</sup> <sup>375</sup> <sup>376</sup> <sup>377</sup> <sup>378</sup> <sup>379</sup> <sup>380</sup> <sup>381</sup> <sup>382</sup> <sup>383</sup> <sup>384</sup> <sup>385</sup> <sup>386</sup> <sup>387</sup> <sup>388</sup> <sup>389</sup> <sup>390</sup> <sup>391</sup> <sup>392</sup> <sup>393</sup> <sup>394</sup> <sup>395</sup> <sup>396</sup> <sup>397</sup> <sup>398</sup> <sup>399</sup> <sup>400</sup> <sup>401</sup> <sup>402</sup> <sup>403</sup> <sup>404</sup> <sup>405</sup> <sup>406</sup> <sup>407</sup> <sup>408</sup> <sup>409</sup> <sup>410</sup> <sup>411</sup> <sup>412</sup> <sup>413</sup> <sup>414</sup> <sup>415</sup> <sup>416</sup> <sup>417</sup> <sup>418</sup> <sup>419</sup> <sup>420</sup> <sup>421</sup> <sup>422</sup> <sup>423</sup> <sup>424</sup> <sup>425</sup> <sup>426</sup> <sup>427</sup> <sup>428</sup> <sup>429</sup> <sup>430</sup> <sup>431</sup> <sup>432</sup> <sup>433</sup> <sup>434</sup> <sup>435</sup> <sup>436</sup> <sup>437</sup> <sup>438</sup> <sup>439</sup> <sup>440</sup> <sup>441</sup> <sup>442</sup> <sup>443</sup> <sup>444</sup> <sup>445</sup> <sup>446</sup> <sup>447</sup> <sup>448</sup> <sup>449</sup> <sup>450</sup> <sup>451</sup> <sup>452</sup> <sup>453</sup> <sup>454</sup> <sup>455</sup> <sup>456</sup> <sup>457</sup> <sup>458</sup> <sup>459</sup> <sup>460</sup> <sup>461</sup> <sup>462</sup> <sup>463</sup> <sup>464</sup> <sup>465</sup> <sup>466</sup> <sup>467</sup> <sup>468</sup> <sup>469</sup> <sup>470</sup> <sup>471</sup> <sup>472</sup> <sup>473</sup> <sup>474</sup> <sup>475</sup> <sup>476</sup> <sup>477</sup> <sup>478</sup> <sup>479</sup> <sup>480</sup> <sup>481</sup> <sup>482</sup> <sup>483</sup> <sup>484</sup> <sup>485</sup> <sup>486</sup> <sup>487</sup> <sup>488</sup> <sup>489</sup> <sup>490</sup> <sup>491</sup> <sup>492</sup> <sup>493</sup> <sup>494</sup> <sup>495</sup> <sup>496</sup> <sup>497</sup> <sup>498</sup> <sup>499</sup> <sup>500</sup> <sup>501</sup> <sup>502</sup> <sup>503</sup> <sup>504</sup> <sup>505</sup> <sup>506</sup> <sup>507</sup> <sup>508</sup> <sup>509</sup> <sup>510</sup> <sup>511</sup> <sup>512</sup> <sup>513</sup> <sup>514</sup> <sup>515</sup> <sup>516</sup> <sup>517</sup> <sup>518</sup> <sup>519</sup> <sup>520</sup> <sup>521</sup> <sup>522</sup> <sup>523</sup> <sup>524</sup> <sup>525</sup> <sup>526</sup> <sup>527</sup> <sup>528</sup> <sup>529</sup> <sup>530</sup> <sup>531</sup> <sup>532</sup> <sup>533</sup> <sup>534</sup> <sup>535</sup> <sup>536</sup> <sup>537</sup> <sup>538</sup> <sup>539</sup> <sup>540</sup> <sup>541</sup> <sup>542</sup> <sup>543</sup> <sup>544</sup> <sup>545</sup> <sup>546</sup> <sup>547</sup> <sup>548</sup> <sup>549</sup> <sup>550</sup> <sup>551</sup> <sup>552</sup> <sup>553</sup> <sup>554</sup> <sup>555</sup> <sup>556</sup> <sup>557</sup> <sup>558</sup> <sup>559</sup> <sup>560</sup> <sup>561</sup> <sup>562</sup> <sup>563</sup> <sup>564</sup> <sup>565</sup> <sup>566</sup> <sup>567</sup> <sup>568</sup> <sup>569</sup> <sup>570</sup> <sup>571</sup> <sup>572</sup> <sup>573</sup> <sup>574</sup> <sup>575</sup> <sup>576</sup> <sup>577</sup> <sup>578</sup> <sup>579</sup> <sup>580</sup> <sup>581</sup> <sup>582</sup> <sup>583</sup> <sup>584</sup> <sup>585</sup> <sup>586</sup> <sup>587</sup> <sup>588</sup> <sup>589</sup> <sup>590</sup> <sup>591</sup> <sup>592</sup> <sup>593</sup> <sup>594</sup> <sup>595</sup> <sup>596</sup> <sup>597</sup> <sup>598</sup> <sup>599</sup> <sup>600</sup> <sup>601</sup> <sup>602</sup> <sup>603</sup> <sup>604</sup> <sup>605</sup> <sup>606</sup> <sup>607</sup> <sup>608</sup> <sup>609</sup> <sup>610</sup> <sup>611</sup> <sup>612</sup> <sup>613</sup> <sup>614</sup> <sup>615</sup> <sup>616</sup> <sup>617</sup> <sup>618</sup> <sup>619</sup> <sup>620</sup> <sup>621</sup> <sup>622</sup> <sup>623</sup> <sup>624</sup> <sup>625</sup> <sup>626</sup> <sup>627</sup> <sup>628</sup> <sup>629</sup> <sup>630</sup> <sup>631</sup> <sup>632</sup> <sup>633</sup> <sup>634</sup> <sup>635</sup> <sup>636</sup> <sup>637</sup> <sup>638</sup> <sup>639</sup> <sup>640</sup> <sup>641</sup> <sup>642</sup> <sup>643</sup> <sup>644</sup> <sup>645</sup> <sup>646</sup> <sup>647</sup> <sup>648</sup> <sup>649</sup> <sup>650</sup> <sup>651</sup> <sup>652</sup> <sup>653</sup> <sup>654</sup> <sup>655</sup> <sup>656</sup> <sup>657</sup> <sup>658</sup> <sup>659</sup> <sup>660</sup> <sup>661</sup> <sup>662</sup> <sup>663</sup> <sup>664</sup> <sup>665</sup> <sup>666</sup> <sup>667</sup> <sup>668</sup> <sup>669</sup> <sup>670</sup> <sup>671</sup> <sup>672</sup> <sup>673</sup> <sup>674</sup> <sup>675</sup> <sup>676</sup> <sup>677</sup> <sup>678</sup> <sup>679</sup> <sup>680</sup> <sup>681</sup> <sup>682</sup> <sup>683</sup> <sup>684</sup> <sup>685</sup> <sup>686</sup> <sup>687</sup> <sup>688</sup> <sup>689</sup> <sup>690</sup> <sup>691</sup> <sup>692</sup> <sup>693</sup> <sup>694</sup> <sup>695</sup> <sup>696</sup> <sup>697</sup> <sup>698</sup> <sup>699</sup> <sup>700</sup> <sup>701</sup> <sup>702</sup> <sup>703</sup> <sup>704</sup> <sup>705</sup> <sup>706</sup> <sup>707</sup> <sup>708</sup> <sup>709</sup> <sup>710</sup> <sup>711</sup> <sup>712</sup> <sup>713</sup> <sup>714</sup> <sup>715</sup> <sup>716</sup> <sup>717</sup> <sup>718</sup> <sup>719</sup> <sup>720</sup> <sup>721</sup> <sup>722</sup> <sup>723</sup> <sup>724</sup> <sup>725</sup> <sup>726</sup> <sup>727</sup> <sup>728</sup> <sup>729</sup> <sup>730</sup> <sup>731</sup> <sup>732</sup> <sup>733</sup> <sup>734</sup> <sup>735</sup> <sup>736</sup> <sup>737</sup> <sup>738</sup> <sup>739</sup> <sup>740</sup> <sup>741</sup> <sup>742</sup> <sup>743</sup> <sup>744</sup> <sup>745</sup> <sup>746</sup> <sup>747</sup> <sup>748</sup> <sup>749</sup> <sup>750</sup> <sup>751</sup> <sup>752</sup> <sup>753</sup> <sup>754</sup> <sup>755</sup> <sup>756</sup> <sup>757</sup> <sup>758</sup> <sup>759</sup> <sup>760</sup> <sup>761</sup> <sup>762</sup> <sup>763</sup> <sup>764</sup> <sup>765</sup> <sup>766</sup> <sup>767</sup> <sup>768</sup> <sup>769</sup> <sup>770</sup> <sup>771</sup> <sup>772</sup> <sup>773</sup> <sup>774</sup> <sup>775</sup> <sup>776</sup> <sup>777</sup> <sup>778</sup> <sup>779</sup> <sup>780</sup> <sup>781</sup> <sup>782</sup> <sup>783</sup> <sup>784</sup> <sup>785</sup> <sup>786</sup> <sup>787</sup> <sup>788</sup> <sup>789</sup> <sup>790</sup> <sup>791</sup> <sup>792</sup> <sup>793</sup> <sup>794</sup> <sup>795</sup> <sup>796</sup> <sup>797</sup> <sup>798</sup> <sup>799</sup> <sup>800</sup> <sup>801</sup> <sup>802</sup> <sup>803</sup> <sup>804</sup> <sup>805</sup> <sup>806</sup> <sup>807</sup> <sup>808</sup> <sup>809</sup> <sup>810</sup> <sup>811</sup> <sup>812</sup> <sup>813</sup> <sup>814</sup> <sup>815</sup> <sup>816</sup> <sup>817</sup> <sup>818</sup> <sup>819</sup> <sup>820</sup> <sup>821</sup> <sup>822</sup> <sup>823</sup> <sup>824</sup> <sup>825</sup> <sup>826</sup> <sup>827</sup> <sup>828</sup> <sup>829</sup> <sup>830</sup> <sup>831</sup> <sup>832</sup> <sup>833</sup> <sup>834</sup> <sup>835</sup> <sup>836</sup> <sup>837</sup> <sup>838</sup> <sup>839</sup> <sup>840</sup> <sup>841</sup> <sup>842</sup> <sup>843</sup> <sup>844</sup> <sup>845</sup> <sup>846</sup> <sup>847</sup> <sup>848</sup> <sup>849</sup> <sup>850</sup> <sup>851</sup> <sup>852</sup> <sup>853</sup> <sup>854</sup> <sup>855</sup> <sup>856</sup> <sup>857</sup> <sup>858</sup> <sup>859</sup> <sup>860</sup> <sup>861</sup> <sup>862</sup> <sup>863</sup> <sup>864</sup> <sup>865</sup> <sup>866</sup> <sup>867</sup> <sup>868</sup> <sup>869</sup> <sup>870</sup> <sup>871</sup> <sup>872</sup> <sup>873</sup> <sup>874</sup> <sup>875</sup> <sup>876</sup> <sup>877</sup> <sup>878</sup> <sup>879</sup> <sup>880</sup> <sup>881</sup> <sup>882</sup> <sup>883</sup> <sup>884</sup> <sup>885</sup> <sup>886</sup> <sup>887</sup> <sup>888</sup> <sup>889</sup> <sup>890</sup> <sup>891</sup> <sup>892</sup> <sup>893</sup> <sup>894</sup> <sup>895</sup> <sup>896</sup> <sup>897</sup> <sup>898</sup> <sup>899</sup> <sup>900</sup> <sup>901</sup> <sup>902</sup> <sup>903</sup> <sup>904</sup> <sup>905</sup> <sup>906</sup> <sup>907</sup> <sup>908</sup> <sup>909</sup> <sup>910</sup> <sup>911</sup> <sup>912</sup> <sup>913</sup> <sup>914</sup> <sup>915</sup> <sup>916</sup> <sup>917</sup> <sup>918</sup> <sup>919</sup> <sup>920</sup> <sup>921</sup> <sup>922</sup> <sup>923</sup> <sup>924</sup> <sup>925</sup> <sup>926</sup> <sup>927</sup> <sup>928</sup> <sup>929</sup> <sup>930</sup> <sup>931</sup> <sup>932</sup> <sup>933</sup> <sup>934</sup> <sup>935</sup> <sup>936</sup> <sup>937</sup> <sup>938</sup> <sup>939</sup> <sup>940</sup> <sup>941</sup> <sup>942</sup> <sup>943</sup> <sup>944</sup> <sup>945</sup> <sup>946</sup> <sup>947</sup> <sup>948</sup> <sup>949</sup> <sup>950</sup> <sup>951</sup> <sup>952</sup> <sup>953</sup> <sup>954</sup> <sup>955</sup> <sup>956</sup> <sup>957</sup> <sup>958</sup> <sup>959</sup> <sup>960</sup> <sup>961</sup> <sup>962</sup> <sup>963</sup> <sup>964</sup> <sup>965</sup> <sup>966</sup> <sup>967</sup> <sup>968</sup> <sup>969</sup> <sup>970</sup> <sup>971</sup> <sup>972</sup> <sup>973</sup> <sup>974</sup> <sup>975</sup> <sup>976</sup> <sup>977</sup> <sup>978</sup> <sup>979</sup> <sup>980</sup> <sup>981</sup> <sup>982</sup> <sup>983</sup> <sup>984</sup> <sup>985</sup> <sup>986</sup> <sup>987</sup> <sup>988</sup> <sup>989</sup> <sup>990</sup> <sup>991</sup> <sup>992</sup> <sup>993</sup> <sup>994</sup> <sup>995</sup> <sup>996</sup> <sup>997</sup> <sup>998</sup> <sup>999</sup> <sup>1000</sup> <sup>1001</sup> <sup>1002</sup> <sup>1003</sup> <sup>1004</sup> <sup>1005</sup> <sup>1006</sup> <sup>1007</sup> <sup>1008</sup> <sup>1009</sup> <sup>1010</sup> <sup>1011</sup> <sup>1012</sup> <sup>1013</sup> <sup>1014</sup> <sup>1015</sup> <sup>1016</sup> <sup>1017</sup> <sup>1018</sup> <sup>1019</sup> <sup>1020</sup> <sup>1021</sup> <sup>1022</sup> <sup>1023</sup> <sup>1024</sup> <sup>1025</sup> <sup>1026</sup> <sup>1027</sup> <sup>1028</sup> <sup>1029</sup> <sup>1030</sup> <sup>1031</sup> <sup>1032</sup> <sup>1033</sup> <sup>1034</sup> <sup>1035</sup> <sup>1036</sup> <sup>1037</sup> <sup>1038</sup> <sup>1039</sup> <sup>1040</sup> <sup>1041</sup> <sup>1042</sup> <sup>1043</sup> <sup>1044</sup> <sup>1045</sup> <sup>1046</sup> <sup>1047</sup> <sup>1048</sup> <sup>1049</sup> <sup>1050</sup> <sup>1051</sup> <sup>1052</sup> <sup>1053</sup> <sup>1054</sup> <sup>1055</sup> <sup>1056</sup> <sup>1057</sup> <sup>1058</sup> <sup>1059</sup> <sup>1060</sup> <sup>1061</sup> <sup>1062</sup> <sup>1063</sup> <sup>1064</sup> <sup>1065</sup> <sup>1066</sup> <sup>1067</sup> <sup>1068</sup> <sup>1069</sup> <sup>1070</sup> <sup>1071</sup> <sup>1072</sup> <sup>1073</sup> <sup>1074</sup> <sup>1075</sup> <sup>1076</sup> <sup>1077</sup> <sup>1078</sup> <sup>1079</sup> <sup>1080</sup> <sup>1081</sup> <sup>1082</sup> <sup>1083</sup> <sup>1084</sup> <sup>1085</sup> <sup>1086</sup> <sup>1087</sup> <sup>1088</sup> <sup>1089</sup> <sup>1090</sup> <sup>1091</sup> <sup>1092</sup> <sup>1093</sup> <sup>1094</sup> <sup>1095</sup> <sup>1096</sup> <sup>1097</sup> <sup>1098</sup> <sup>1099</sup> <sup>1100</sup> <sup>1101</sup> <sup>1102</sup> <sup>1103</sup> <sup>1104</sup> <sup>1105</sup> <sup>1106</sup> <sup>1107</sup> <sup>1108</sup> <sup>1109</sup> <sup>1110</sup> <sup>1111</sup> <sup>1112</sup> <sup>1113</sup> <sup>1114</sup> <sup>1115</sup> <sup>1116</sup> <sup>1117</sup> <sup>1118</sup> <sup>1119</sup> <sup>1120</sup> <sup>1121</sup> <sup>1122</sup> <sup>1123</sup> <sup>1124</sup> <sup>1125</sup> <sup>1126</sup> <sup>1127</sup> <sup>1128</sup> <sup>1129</sup> <sup>1130</sup> <sup>1131</sup> <sup>1132</sup> <sup>1133</sup> <sup>1134</sup> <sup>1135</sup> <sup>1136</sup> <sup>1137</sup> <sup>1138</sup> <sup>1139</sup> <sup>1140</sup> <sup>1141</sup> <sup>1142</sup> <sup>1143</sup> <sup>1144</sup> <sup>1145</sup> <sup>1146</sup> <sup>1147</sup> <sup>1148</sup> <sup>1149</sup> <sup>1150</sup> <sup>1151</sup> <sup>1152</sup> <sup>1153</sup> <sup>1154</sup> <sup>1155</sup> <sup>1156</sup> <sup>1157</sup> <sup>1158</sup> <sup>1159</sup> <sup>1160</sup> <sup>1161</sup> <sup>1162</sup> <sup>1163</sup> <sup>1164</sup> <sup>1165</sup> <sup>1166</sup> <sup>1167</sup> <sup>1168</sup> <sup>1169</sup> <sup>1170</sup> <sup>1171</sup> <sup>1172</sup> <sup>1173</sup> <sup>1174</sup> <sup>1175</sup> <sup>1176</sup> <sup>1177</sup> <sup>1178</sup> <sup>1179</sup> <sup>1180</sup> <sup>1181</sup> <sup>1182</sup> <sup>1183</sup> <sup>1184</sup> <sup>1185</sup> <sup>1186</sup> <sup>1187</sup> <sup>1188</sup> <sup>1189</sup> <sup>1190</sup> <sup>1191</sup> <sup>1192</sup> <sup>1193</sup> <sup>1194</sup> <sup>1195</sup> <sup>1196</sup> <sup>1197</sup> <sup>1198</sup> <sup>1199</sup> <sup>1200</sup> <sup>1201</sup> <sup>1202</sup> <sup>1203</sup> <sup>1204</sup> <sup>1205</sup> <sup>1206</sup> <sup>1207</sup> <sup>1208</sup> <sup>1209</sup> <sup>1210</sup> <sup>1211</sup> <sup>1212</sup> <sup>1213</sup> <sup>1214</sup> <sup>1215</sup> <sup>1216</sup> <sup>1217</sup> <sup>1218</sup> <sup>1219</sup> <sup>1220</sup> <sup>1221</sup> <sup>1222</sup> <sup>1223</sup> <sup>1224</sup> <sup>1225</sup> <sup>1226</sup> <sup>1227</sup> <sup>1228</sup> <sup>1229</sup> <sup>1230</sup> <sup>1231</sup> <sup>1232</sup> <sup>1233</sup> <sup>1234</sup> <sup>1235</sup> <sup>1236</sup> <sup>1237</sup> <sup>1238</sup> <sup>1239</sup> <sup>1240</sup> <sup>1241</sup> <sup>1242</sup> <sup>1243</sup> <sup>1244</sup> <sup>1245</sup> <sup>1246</sup> <sup>1247</sup> <sup>1248</sup> <sup>1249</sup> <sup>1250</sup> <sup>1251</sup> <sup>1252</sup> <sup>1253</sup> <sup>1254</sup> <sup>1255</sup> <sup>1256</sup> <sup>1257</sup> <sup>1258</sup> <sup>1259</sup> <sup>1260</sup> <sup>1261</sup> <sup>1262</sup> <sup>1263</sup> <sup>1264</sup> <sup>1265</sup> <sup>1266</sup> <sup>1267</sup> <sup>1268</sup> <sup>1269</sup> <sup>1270</sup> <sup>1271</sup> <sup>1272</sup> <sup>1273</sup> <sup>1274</sup> <sup>1275</sup> <sup>1276</sup> <sup>1277</sup> <sup>1278</sup> <sup>1279</sup> <sup>1280</sup> <sup>1281</sup> <sup>1282</sup> <sup>1283</sup> <sup>1284</sup> <sup>1285</sup> <sup>1286</sup> <sup>1287</sup> <sup>1288</sup> <sup>1289</sup> <sup>1290</sup> <sup>1291</sup> <sup>1292</sup> <sup>1293</sup> <sup>1294</sup> <sup>1295</sup> <sup>1296</sup> <sup>1297</sup> <sup>1298</sup> <sup>1299</sup> <sup>1300</sup> <sup>1301</sup> <sup>1302</sup> <sup>1303</sup> <sup>1304</sup> <sup>1305</sup> <sup>1306</sup>

was formed. In this examination, the relationships between a depth from the surface of the silicon-containing insulating film 111 and a Cu (copper) concentration at that depth were examined. <sup>The</sup> [An] abscissa

5 in FIG.3 denotes the depth (nm) from the surface of the insulating film 111 <sup>on</sup> in a linear scale, and <sup>the</sup> an ordinate on the left side denotes the Cu (copper) concentration (atoms/cc, i.e., the number of atoms per 1 cc) <sup>on</sup> in a logarithmic scale. In this examination, secondary ion intensity (cts/sec) of Si (silicon) and C (carbon) contained in the film were also examined. <sup>The</sup> An ordinate on the right side of the FIG.3 denotes the secondary ion intensity (cts/sec) of Si (silicon) and C (carbon) <sup>on</sup> in a logarithmic scale.

15 In FIG.3, the numerical value affixed to the left side of the symbol of <sup>an</sup> elements indicates the mass number of this element.

[Also,] FIG.4 is a graph showing <sup>content of</sup> [SIMS examination] <sup>of</sup> the elements <sup>that were</sup> contained in the silicon-containing insulating film 111 <sup>versus depth</sup> after the silicon-containing insulating film 111 examined in FIG.3 was annealed in vacuum at 500 °C for 4 hours. This examination was carried out in <sup>a manner</sup> [the] similar [way] to that in FIG.3.

25 Focusing on the copper concentration at <sup>a</sup> the depth of 60 to 80 nm in FIG.4 reveals that gradient of the graph in this region is relatively steep, which indicate <sup>5</sup> that <sup>little</sup>



copper diffusion<sup>ed</sup> from the copper wiring 110 into the insulating film 111 is little.

In addition, as shown in FIG.4, Cu (copper) contained in the silicon-containing insulating film 111 is very small in the middle range (the depth of about 20 to 60 nm) of the film. <sup>In practice</sup> Practically, it is preferable that the number of Cu<sup>atoms</sup> in the middle range of the film is <sup>be</sup> less than  $10^{17}$ . It can be seen that the present method fulfills this condition.

<sup>The foregoing</sup> Above arguments shows that the present invention can prevent the copper diffusion even when the anneal<sup>ing</sup> is performed.

Next, in order to further confirm the effect of the N<sub>2</sub> plasma process, the ~~explanation will be made for the~~ case where the N<sub>2</sub> plasma <sup>treatment</sup> process is ~~not executed~~ <sup>omitted will be explained</sup> with reference to FIG.5 and FIG.6 hereunder. FIG.5 is a graph showing SIMS examination results, obtained immediately after the silicon- containing insulating film 111 was formed, <sup>for</sup> about the elements that were contained in the silicon- containing insulating film 111 that was not subjected to the N<sub>2</sub> plasma <sup>treatment</sup> process. This <sup>In this</sup> is just the case <sup>only</sup> where the step shown in FIG.2C is executed, without executing the step in FIG.2B, directly after the step shown in FIG.2A is executed. Also, FIG.6 is a graph showing SIMS examination <sup>the</sup> results <sup>of</sup> about <sup>for</sup> the elements that were contained in the insulating film 111 of the FIG.5, which <sup>was</sup> were further subjected to an annealing in vacuum at

500 °C for 4 hours.

In FIG.5 and FIG.6, <sup>the</sup> an abscissa denotes [a] depth (nm) from the surface of the insulating film 111 <sup>on</sup> in a linear scale. <sup>The</sup> [Then, an] ordinate on the left side denotes the Cu (copper) concentration (atoms/cc) <sup>on</sup> in a logarithmic scale. [Also, <sup>The</sup> an] ordinate on the right side denotes secondary ion intensity (cts/sec) of Si (silicon), C (carbon), and F (fluorine) <sup>on</sup> in a logarithmic scale [respectively].

As is apparent from comparing the Cu (copper) concentration of FIG.5 (before the annealing) and that of FIG.6 (after the annealing), it can be understood that <sup>the</sup> <sup>annealing causes</sup> the copper of the copper wiring layer 110 <sup>to</sup> diffuses into the silicon-containing insulating film 111. [by the annealing]

On the other hand, comparing the Cu (copper) of FIG.4 (<sup>with</sup> performing the N<sub>2</sub> plasma <sup>treatment</sup> process) and that of FIG.6 (<sup>without</sup> ~~not performing~~ the N<sub>2</sub> plasma <sup>treatment</sup> process) reveals the effect of the plasma [treatment process]. That is, it can be understood that the Cu (copper) concentration in FIG.4 is lower than that in FIG.6.

[According to the examination] <sup>the</sup> results shown in FIG.3 to FIG.6, [it was] <sup>is</sup> verified that if the surface of the copper wiring layer 110 [was] exposed to the plasma under the conditions A, <sup>2</sup> [the] <sup>3</sup> surface [layer] portion of the copper wiring layer 110 [was] reformed to functions <sup>a</sup> as [the] copper diffusion preventing layer. The inventors speculates that the surface [layer] portion of the copper wiring layer

110 <sup>is</sup> [would be] nitrided by the plasma process and thus a thin film <sup>is</sup> [made] of copper nitride <sup>from</sup> [would be] formed <sup>on</sup> the surface [layer] portion, and this thin film [would] serve as <sup>a</sup> [the] copper diffusion preventing layer.

5 This means that the copper wiring layer 110 itself [have the] function <sup>to</sup> [of] preventing <sup>embodiment</sup> [the] copper diffusion. Therefore, according to the first <sup>embodiment</sup> method, there is no need <sup>for</sup> [to require] the copper diffusion preventing film formed on the copper wiring layer 110 to have superior ability <sup>in</sup> [of] preventing the copper diffusion. For this reason, there is no need in the first <sup>embodiment</sup> <sup>for</sup> method to employ <sup>a</sup> [the] high dielectric constant film such as the SiN film [that is] employed in the prior art <sup>for</sup> [due to] its superior ability <sup>in</sup> [of] preventing the copper diffusion.

15 <sup>Embodiment</sup> (2) Second <sup>embodiment</sup> method <sup>now</sup> Next, the second <sup>embodiment</sup> method will be explained with reference to FIGS. 7A to 7C <sup>embodiment</sup> hereunder.

In this <sup>embodiment</sup> method, as shown in FIG. 7A, a substrate 103 is loaded on the lower electrode 102 (see FIG. 1). The substrate 103 <sup>has a</sup> is constructed by forming the copper wiring layer 110 <sup>formed on</sup> on <sup>an</sup> [the] underlying insulating film 112 <sup>in turn,</sup> which [Although not shown, the underlying insulating film 112] is formed on a silicon substrate.

25 Then, as shown in FIG. 7B, the silicon-containing insulating film 111 <sup>with a</sup> [whose] film thickness <sup>is</sup> [is] 100 nm is formed on the copper wiring layer 110. This silicon-containing insulating film 111 is formed by the CVD

method in accordance with the conditions B <sup>given above for</sup> explained in the first method.

In turn, as shown in FIG.7C, the surface of the silicon- containing insulating film 111 is reformed by the plasma process in accordance with following conditions C.

(Conditions C)

- temperature of the substrate 103: ~~10~~ 375 °C
- pressure in the chamber 101: ~~10~~ 0.5 to 6.0 Torr
- 10 • power of the first high frequency power supply 107: ~~10~~ 0 W (not applied)
- frequency of the second high frequency power supply 109: ~~10~~ 380 KHz
- power of the second high frequency power supply 15 109: ~~10~~ 150 W
- process time: ~~10~~ 30 sec
- process gas flow rate: ~~10~~ see Table 3

Table 3

	Process gas	gas flow rate (sccm)
20	① NH <sub>3</sub>	100 to 300
	② N <sub>2</sub>	100 to 300
	③ N <sub>2</sub> O	100 to 300

At least one of NH<sub>3</sub>, N<sub>2</sub>, and N<sub>2</sub>O in Table 3 may be employed as the process gas.

25 Though only the second high frequency power supply 109 is employed under the conditions C, the first high frequency power supply 107 may be employed together with

the second high frequency power supply 109. Alternatively, the first high frequency power supply 107 may be employed without employing the second high frequency power supply 109.

5           Next, <sup>the</sup> examination <sup>of</sup> results <sup>of</sup> [about] <sup>of</sup> [the] copper diffusion from the copper wiring layer 110 into the silicon-containing insulating film 111 will be explained with reference to FIG.8 [hereunder]. <sup>In</sup> <sup>particular</sup> [y], the [explanation will be made for] the case where the SiOCH film (see ① in Table 2) is used as the silicon-containing insulating film 111, and NH<sub>3</sub> (see ① in Table 3) is used as the process gas <sup>under</sup> <sup>the results of</sup> <sup>will be explained,</sup> in the conditions C.

FIG.8 is a graph showing <sup>the results of</sup> SIMS examination [results] <sup>of</sup> [about] the relationships between the depth (nm) from the surface of the silicon-containing insulating film 111 and the Cu (copper) concentration (atoms/cc) at that depth, when the insulating film 111 is annealed in vacuum at 450 °C for 4 hours after subjected to the NH<sub>3</sub> plasma process. [In this examination, <sup>embodiment</sup> as in the first [method], the relationships between the depth (nm) from the surface of the insulating film 111 and the secondary ion intensity (cts/sec) of Si (silicon) and C (carbon) at that depth were also examined. The SIMS examination method <sup>was</sup> <sup>employed</sup> <sup>embodiment</sup> is similar to that <sup>there is little</sup> in the first [method].

25           As shown in FIG.8, <sup>embodiment</sup> [the] diffusion of Cu (copper) [is] <sup>little</sup> in this [method]. In addition, it can be understood from comparing FIG.6 <sup>without</sup> [not executing] the NH<sub>3</sub> plasma

process) and FIG.8 <sup>with</sup> (executing) the  $\text{NH}_3$  plasma process), that the Cu (copper) concentration in FIG.8 <sup>with</sup> (executing) the  $\text{NH}_3$  plasma process <sup>is executed</sup> is lower.

5 This <sup>Thus,</sup> means that exposing the surface of the silicon-containing insulating film 111 allows the film 111 to be reformed and to <sup>25</sup> <sup>2</sup> have a function <sup>of</sup> copper diffusion preventing film.

In this example, <sup>2</sup> the SiOCH film is employed as the silicon-containing insulating film 111 and this film is  
10 formed by using <sup>2</sup> the reaction gas containing the HMDSO (see the conditions B). Therefore, as has already been explained, not only the dielectric constant of the film can be lowered to about 4 but also the leakage current can be suppressed.

No 15 <sup>41</sup> The inventors actually measured this leakage current. FIG.9 shows a sectional structure <sup>which illustrates</sup> <sup>used to</sup> measure <sup>ment as</sup> the leakage current. In FIG.9, 202 denotes a p-type silicon substrate that is grounded. Then, the silicon-containing insulating film 111 was formed on this  
20 p-type silicon substrate 202 under the conditions B. Also, 201 denotes a mercury probe used to apply the test voltage to the silicon-containing insulating film 111.

Measured results are shown in FIG.10 and FIG.11. In these figures, <sup>the</sup> an abscissa denotes <sup>an</sup> electric field strength (MV/cm) applied to the mercury probe 201 (see  
25 FIG.9) <sup>on</sup> in the measurement <sup>a</sup> in a linear scale. A minus sign in the abscissa shows that <sup>a</sup> the negative voltage is

applied to the mercury probe 201. <sup>The</sup> An ordinate denotes the leakage current ( $A/cm^2$ ) <sup>on</sup> in a logarithmic scale.

FIG.10 is a graph showing the leakage current in the insulating film 111 when the  $NH_3$  plasma <sup>treatment</sup> process (under the conditions C) was performed for the insulating film 111 immediately after the insulating film 111 was formed.

On the other hand, FIG.11 is a graph showing the leakage current of the insulating film 111 after it was subjected to the  $NH_3$  plasma <sup>treatment</sup> process (under the conditions C) and was then annealed. The annealing was carried out in vacuum at  $450^\circ C$  for 4 hours.

As is apparent from comparing FIG.10 and FIG.11, <sup>it</sup> is understood that the leakage current characteristic of the insulating film 111 that is subjected to the  $NH_3$  plasma <sup>treatment is</sup> process is seldom changed <sup>by</sup> before and after the annealing. Focusing on the curve A in FIG.10 and FIG.11 shows that the curve A shifts to the left side (higher electric field side) when the annealing <sup>is</sup> performed (FIG.11). Therefore, it can be expected that the leakage current characteristic can be improved by the annealing.

As described above, according to this <sup>embodiment</sup> method, the copper diffusion can be prevented by the silicon-containing insulating film 111 whose dielectric constant is lower <sup>that as</sup> than the prior art and in which the leakage current <sup>is</sup> can be suppressed. Since the dielectric constant is lower than the prior art, insulating film 111 does not have <sup>the</sup> a problem of lowering the operating speed of the

semiconductor device as in the prior art.

It should be noted that the first and the second <sup>embodiments</sup> ~~method~~ may be executed independently as in the above or in combination thereof. Combining the first and the second <sup>embodiments</sup> ~~method~~ leads to the same advantage<sup>s</sup> as <sup>described</sup> ~~in the~~ above.

③ Explanation ~~of the method~~ of removing the natural oxide film <sup>from</sup> on the surface of the copper wiring layer 110

The first and the second <sup>embodiments</sup> ~~methods~~ explained above may be executed after the natural oxide film on the surface of the copper wiring layer 110 is removed. This prevents the silicon-containing insulating film 111 from peeling off from the copper wiring layer 110. In order to remove the natural oxide film of the copper wiring layer 110 in the present embodiment<sup>s</sup>, the surface of the copper wiring layer 110 is exposed to the NH<sub>3</sub> plasma. The NH<sub>3</sub> plasma process conditions are given <sup>as the</sup> ~~in~~ following conditions D.

(Conditions D)

NH<sub>3</sub> flow rate <sup>1</sup>/<sub>1</sub> 500 sccm  
 temperature of the substrate 103<sup>1</sup>/<sub>1</sub> 75 °C  
 pressure in the chamber 101<sup>1</sup>/<sub>1</sub> 6.0 Torr  
 frequency of the first high frequency power supply  
 107<sup>1</sup>/<sub>1</sub> 13.56 MHz  
 power of the first high frequency power supply  
 107<sup>1</sup>/<sub>1</sub> 400 W  
 power of the second high frequency power supply



109.440 W (not applied)

process time 10 sec

(3) Explanation of application Examples of the present invention

5 Next, Application examples of the present invention will be explained hereunder. In the following, the present invention is applied to the damascene method that is useful for forming the copper wiring layer. FIGS. 12A to 12H are sectional views showing the case where the present invention is applied to the damascene method.

10 Firstly, as shown in FIG. 12A, the substrate 103 is prepared. This substrate 103 <sup>consists of</sup> is constructed by forming the copper wiring layer (lower wiring) 110 <sup>formed</sup> on the underlying insulating film 112, such as <sup>the</sup> SiO<sub>2</sub> film, [etc.]. <sup>which, in turn,</sup> Although not shown, the underlying insulating film 112 is formed on the silicon substrate.

15 Then, as shown in FIG. 12B, in order to remove the natural oxide film <sup>from</sup> on the surface of the copper wiring layer 110, the surface is exposed to the NH<sub>3</sub> plasma. The conditions for the NH<sub>3</sub> plasma process are [given as] the conditions D <sup>given</sup> Explained above.

20 Then, as shown in FIG. 12C, the surface of the copper wiring layer 110, whose natural oxide film <sup>has been</sup> is removed, is [processed by] <sup>treated with</sup> the plasma. The conditions for this plasma process are given as the conditions A explained [in the] above <sup>in connection with the</sup> first <sup>embodiment</sup> method. The surface layer portion of the copper wiring layer 110 is reformed by this plasma

<sup>treatment</sup>  
[process], and this surface layer portion functions as the  
copper diffusion <sup>barrier</sup> ~~preventing layer~~.

In turn, as shown in FIG.12D, the silicon-containing  
insulating film 111 is formed on the copper wiring layer  
5 110. This silicon-containing insulating film 111 is  
formed under the conditions B explained above. Since the  
silicon-containing insulating film 111 functions as the  
block insulating film in the present <sup>referred to as</sup> ~~application~~ example,  
the insulating film 111 is <sup>referred to as</sup> ~~called as the~~ block insulating  
10 film 111 in the following. Also, because the natural  
oxide film of the copper wiring layer 110 <sup>has been</sup> ~~is~~ removed in  
the step shown in FIG.12B, the block insulating film 111  
is ~~made to be~~ difficult to peel off from the copper  
wiring layer 110. ✓

15 As explained <sup>embodiment</sup> ~~for the~~ above second ~~method~~, after the  
block insulating film 111 is formed, the surface of the  
insulating film 111 may be exposed to the plasma in  
accordance with the above conditions C. In this case,  
the plasma <sup>treatment shown</sup> ~~process~~ in FIG.12C may be omitted. Since the  
20 block insulating film 111 subjected to the plasma <sup>treatment</sup> ~~process~~  
has the function <sup>of</sup> ~~for~~ preventing the diffusion of copper,  
there is no possibility that the copper <sup>will</sup> ~~diffuses~~ into the  
interlayer insulating film <sup>later</sup> ~~to be~~ formed on the insulating  
film 111, even if the plasma <sup>treatment of</sup> ~~process in~~ FIG.12C is omitted.

25 Then, as shown in FIG.12E, the interlayer insulating  
film 113 of low dielectric constant is formed on the  
block insulating film 111, and a protection film 114 is

formed thereon. The interlayer insulating film 113 may  
 be the well-known FSG (Fluorinated Silicon Oxide) or ~~the~~<sup>2</sup>  
 porous SiO<sub>2</sub> film, for example. As the protection film  
 114, ~~the~~<sup>a</sup> NSG film (the silicon oxide film not containing  
 5 ~~the~~ impurity<sup>b</sup>) that has a thin thickness and a high  
 density is employed. If the protection film 114 is  
~~absent~~<sup>omitted</sup>, the quality of the interlayer insulating film 113  
 is altered by the process gas <sup>used in</sup> ~~for~~ ashing<sup>the</sup> photoresist 115  
 (described later) or by <sup>the</sup>etching gas <sup>used for</sup> ~~for~~ etching the block  
 10 insulating film 111 which lies under the interlayer  
 insulating film 113, <sup>and</sup> ~~which degrade~~ the low dielectric  
 constant characteristic of the insulating film 113. <sup>is thereby degraded</sup> If,  
 however, this is not problematic, the protection film 114  
 may be dispensed with.

15 Then, as shown in FIG.12F, the photoresist 115 is  
 coated on the protection film 114, and then an opening  
~~portion~~<sup>115a</sup> is formed in the photoresist 115 by ~~the~~  
 photolithography. Then, an opening ~~portion~~<sup>113a</sup> reaching <sup>down to</sup>  
 the block insulating film 111 is formed by etching the  
 20 interlayer insulating film 113 and the protection film  
 114 via the opening ~~portion~~<sup>115a</sup>, <sup>using</sup> ~~by~~ virtue of ~~the~~  
 reactive ion etching (RIE).

<sup>No P<sub>2</sub></sup> In this etching,<sup>3</sup> gas mixture of CF<sub>4</sub>+CHF<sub>3</sub> is employed  
 as the etching gas, and the block insulating film 111 has  
 25 ~~the~~ etching resistance against this etching gas. In  
 other words, the block insulating film 111 functions as  
 the etching stopper film ~~for~~ this etching.

Then, as shown in FIG.12G, after ashing and removing the photoresist 115, an opening portion 111a reaching <sup>to</sup> the copper wiring layer 110 is formed by etching the block insulating film 111 via the opening portion 113a. This etching is carried out by the reactive ion etching (RIE). In this etching, <sup>a</sup> gas mixture of the  $CF_4 + CHF_3$ , which is employed in etching the interlayer insulating film 113 but whose composition <sup>component</sup> ratio is changed, is employed as the etching gas. Since the copper wiring layer 110 has the etching resistance against this etching gas, the copper wiring layer 110 is not etched by this etching. <sup>In</sup> According to this step, a via hole 116 defined by the opening portion 111a and 113a is formed.

Then, as shown in FIG.12H, a seed layer 117 made of copper is formed on inner walls of the via hole 116 and on the protection film 114 by sputtering. After this, a first electrolytically copper-plated film 118 is formed on the seed layer 117 by supplying <sup>applying</sup> the electrical power to this seed layer 117. Then, the first electrolytically copper-plated film 118 that is formed <sup>above</sup> higher than the via hole 116 is removed by the CMP method (Chemical Mechanical Polishing method). According to these steps, <sup>is formed</sup> the structure in which the plug formed of the first electrolytically copper-plated film 118 is buried in the via hole 116 can be obtained.

Finally, a second electrolytically copper-plated <sup>copper</sup> film (upper wiring) 119 is formed on the seed layer 117

and on the first electrolytically copper-plated film 118 by supplying [the] electrical power to the seed layer 117 once again.

5 Following the above steps leads to a structure [.] in which the copper wiring layer (lower wiring) 110 and the electrolytically [copper]<sup>copper</sup> plated [.] film (upper wiring) 119 are separated by the interlayer insulating film 113, but are electrically connected via the plug.

10 As <sup>has</sup> [is] <sup>been</sup> already explained, when the plasma <sup>treatment</sup> [process] is <sup>applied to</sup> [performed for] the surface of the copper wiring layer (lower wiring) 110 in accordance with the above conditions A, the surface layer portion of the copper wiring layer (lower wiring) 110 is reformed <sup>into a</sup> [to act as the] copper diffusion preventing layer. As a result, there is

15 no need to employ the SiN film of the prior art, which has the high dielectric constant, as the block insulating film 111 formed on the copper wiring layer (lower wiring) 110. Instead, according to the present invention, films listed in Table 2 can be employed. Among these films,

20 SiOCH film and the SiONCH film, <sup>of which</sup> both [are] formed using [the] HMDSO, suppress the leakage current and have a low dielectric constant (about 4.0). Therefore, present example can provide <sup>a</sup> [the] semiconductor device having [the] high operation <sup>a</sup> speed.

25 To summarize, according to the semiconductor device manufacturing method of the present invention, <sup>a</sup> [the] process gas containing any one of N<sub>2</sub> and N<sub>2</sub>O is

<sup>converted to a plasma</sup>  
 [plasmanized] and then the surface of the copper wiring  
 layer is exposed to the [plasmanized] process gas<sup>plasma</sup>.  
 Alternatively, <sup>2</sup> [the] process gas containing  $N_2$  and  $NH_3$  is  
 [plasmanized] in place of this gas<sup>converted to a plasma</sup> and then <sup>contacted with</sup> the surface of  
 5 the copper wiring layer [is exposed to the plasmanized]  
 [process gas]. By these plasma processes, the surface  
 layer portion of the copper wiring layer can be reformed  
 and made into <sup>3</sup> [the] copper diffusion preventing layer.  
 [According to this,] <sup>3</sup> since the copper wiring layer itself  
 10 [has the] function <sup>3</sup> of preventing the copper diffusion, [the]  
 superior <sup>superior capability for</sup> ability of preventing copper diffusion is not  
 required for the copper diffusion preventing film, such  
 as the block insulating film <sup>or</sup> and the like, which is  
 formed on the copper wiring layer. Therefore, there is  
 15 no need to use high dielectric constant films, such as  
 SiN film, which are used in the prior art [due] <sup>for their</sup> to its  
 superior ability <sup>to</sup> of preventing the copper diffusion.

[Then,] <sup>4</sup> If the surface of this copper wiring layer is  
 exposed to the  $NH_3$  plasma before the surface layer  
 20 portion of the copper wiring layer is reformed, the  
 natural oxide film formed on the surface of the copper  
 wiring can be removed.

Also, instead of reforming the surface of the copper  
 wiring layer as above, the silicon-containing insulating  
 25 film may be formed on the copper wiring layer, and then  
 the process gas containing at least one of  $NH_3$ ,  $N_2$ , and  
 $N_2O$  is <sup>converted to a plasma</sup> [plasmanized], and then the surface of the silicon-

containing insulating film may be exposed to the <sup>plasma of the</sup> plasmanized process gas. <sup>In manner</sup> According to this, the silicon-containing insulating film is reformed to act as <sup>a</sup> the copper diffusion preventing film.

5 In this case, if the silicon-containing insulating film is formed by the chemical vapor deposition method using <sup>a</sup> the reaction gas that contains <sup>a</sup> the compound having <sup>a</sup> the siloxane bonds, such silicon-containing insulating film can have <sup>a</sup> low dielectric constant and <sup>a</sup> can suppress  
10 the leakage current. As a result, this silicon-containing insulating film does not have <sup>the</sup> a problem that the leakage current increases as in the prior art and <sup>a</sup> that the operation speed of the semiconductor device is <sup>a</sup> not slowed due to the high dielectric constant as <sup>with</sup> in the SiN  
15 film.

Although the invention has been described with reference to specific embodiments, these descriptions are not meant to be <sup>construed</sup> constructed in a limiting sense. Various modifications of the disclosed embodiments, as well as  
20 alternative embodiments of the invention will become apparent to persons skilled in the art upon reference to the description of the invention. It should be appreciated by those skilled in the art that the conception and the specific embodiment <sup>s</sup> disclosed may be  
25 readily utilized as a basis for modifying or designing other structures for carrying out the <sup>s</sup> same purposes of the present invention. It should also be realized by

those skilled in the art that such equivalent constructions do not depart from the spirit and scope of the invention as set forth in the appended claims.

5 It is therefore contemplated that the claims will cover any such modifications or embodiments that fall within the true scope of the invention.

No ④